Mathematical Modeling of Refining of Stainless Steel in Smelting Reduction Converter Using Chromium Ore

Yan LIU,¹⁾ Mao-Fa JIANG,²⁾ Li-Xian XU²⁾ and De-Yong WANG²⁾

1) The Liaoning Provincial Key Laboratory of Advanced Materials & Preparation Technology, Shenyang University, Shenyang, Liaoning, 110044 China. 2) School of Materials and Metallurgy, Northeastern University, Shenyang, Liaoning, 110004 China.

(Received on August 3, 2011; accepted on November 4, 2011)

For predicting and controlling the process of chromium ore smelting reduction in a converter preferably, the coupling dynamic model is established for the first time based on the kinetic models of chromium ore dissolution and interfacial reducing reaction between the slag and the metal. It can decrease the refining time considerably and improve the production efficiency for producing 12 wt% Cr stainless steel crude melts in a converter when the initial hot metal contains the definite chrome metal at 1560°C. Under the conditions of the mathematical model, the effect of chromium ore size on the process of producing stainless steel crude melts by chromium ore smelting reduction in a converter is great when the particle size of chromium ore increases to a certain value. In such condition, the dissolution of chromium ore in the slag is the rate controlling step at a certain stage of refining and the rate of chromium ore smelting reduction is controlled jointly by the dissolution and the reduction of chromium ore. The effect of temperature on the process of chromium ore smelting reduction in a converter is significant. The mean reduction rate of chromium ore increases from 0.052 wt%·min⁻¹ to 0.175 wt%·min⁻¹ with the increasing of temperature from 1540°C to 1580°C.

KEY WORDS: mathematical model; smelting reduction; stainless steel; chromium ore; converter.

1. Introduction

Chromium is one of the most important alloying elements in steel production and is often added into the steel as ferrochromium alloy for the production of stainless steel and other alloyed steels. But the decrease of chromium sources makes the price of ferrochromium alloy higher and higher. Along with the development of new technologies, such as the smelting reduction, the hot metal pretreatment and the top and bottom combined blowing converter, it becomes possible to produce stainless steel crude melts by chromium ore powder smelting reduction and direct alloying in a converter. The advantages of the process are as follows: (1) improving the flexibility of choosing main raw materials and direct use of chromium ore powder (2) the use of cheap hot metal, saving electric power and alleviating the scarcity of scrap (3) improving the production efficiency and decreasing the production cost (4) protecting environment.

To reflect the smelting reduction mechanism more specifically, the reasonable reaction models should be developed to describe the process of the smelting reduction. Soykan *et al.*¹⁾ presented a kinetic model that satisfactorily described the solid-state carbothermic reduction of chromite. The model included the contribution of the interfacial area between the partially reduced zone and the unreduced zones in chromite particles and of diffusion. It was observed that at a given particle size, the rate of reduction was controlled mainly by the interfacial area up to the reduction rate about

40%, after which the rate was dominated by diffusion. On the other hand, for a given degree of reduction, the contribution of the interfacial area to the rate increased, while that of diffusion decreased, with a decrease in the particle size. Vercruyssen *et al.*²⁾ described the smelting of stainless steel in a converter with a mathematical model. The smelting process consisted of a primary decarbonization stage and a slag reduction stage. Reactions during the stages involved the metal, the slag and the gas phases. So the model took the three possible interfaces into account in order to simulate the actual reaction mechanisms. Comparison between computed results and industrial process data demonstrated the validity of the model. The SELF-SReM4 is a high order sub-regular solution model, which was used to calculate the component activities of C–Cr–Fe–Ni quaternary system by Zhang *et al.*³⁾ The evaluated component activities were used to predict the bath smelting reduction process of stainless steel crude melts. It was emphasized that the converting temperature must be calculated under the effect of post combustion.

Little work about the reaction kinetic model for the production of stainless steel by chromium ore smelting reduction and direct alloying has been done.^{1,2,4,5)} And there is no way to predict and control accurately the process. So the synthetic kinetic model including a dissolution model and a reduction model of chromium ore should be built to discuss the optimum kinetic conditions for the process.

Against this background, the coupling dynamic model

including a dissolution model and a reduction model for the process of chromium ore smelting reduction in a converter is established for the first time in this paper, and the effect of particle size of chromium ore on the smelting reduction process is discussed.

2. Dynamic Model for Interfacial Reaction between Slag and Metal

In the process of smelting reduction, the interfacial reaction process between slag and metal is dominant and the reaction rate is fast.⁶⁾ The process is the coupling of mass transfer process of each component and chemical reaction process. Therefore, the establishment of the dynamic model is necessary so as to resolve the process of interfacial reaction between slag and metal of stainless steelmaking by chromium ore smelting reduction in a converter.

2.1. Elementary Steps and Rate Controlling Link of Reaction Process

It is assumed that the reaction is composed of the following five steps basing on double-film theory.

(1) Mass transfer of carbon in metal from the interior of molten metal to the interface and diffuseness in the boundary layer of metal side.

(2) Mass transfer of Cr_2O_3 from the interior of molten slag to the interface and diffuseness in the boundary layer of slag side.

(3) Chemical reaction at the interface between slag and metal.

(4) Diffuseness to the metal melt of Cr generated at the interface between slag and metal.

(5) Nucleation and escape process of CO bubble.

The studies in the past⁷⁻¹⁰⁾ indicated that the interfacial reaction process between slag and metal may be controlled by the mass transfer of Cr_2O_3 in slag, the chemical reaction at the interface and the diffuseness of Cr in the boundary layer of metal side respectively, or by them together.

2.2. Integrated Reaction Rate Equations under Various Conditions

(1) Mass transfer of Cr_2O_3 in slag as the rate controlling step

Basing on the Fick's first law and the double-film theory, the mass transfer equation is:

$$\frac{dn_{\text{Cr}_2\text{O}_3}}{dt} = Fk_s(C_{\text{Cr}_2\text{O}_3} - C_{\text{Cr}_2\text{O}_3,i}) \quad (2)$$

where, $n_{\text{Cr}_2\text{O}_3}$ is the mole number of Cr_2O_3 in slag, mol, t is the time, s, F is the interfacial area between slag and metal, m^2 , k_s is the mass transfer coefficient of Cr_2O_3 in slag, $\text{m}\cdot\text{s}^{-1}$, $C_{\text{Cr}_2\text{O}_3,i}$, $C_{\text{Cr}_2\text{O}_3}$ is the molar concentration of Cr_2O_3 at the interface and in slag respectively, $\text{mol}\cdot\text{m}^{-3}$.

In addition, the metal is considered to be saturated with carbon all along in the whole process of chromium ore smelting reduction, namely:¹¹⁾

$$[\%C] = [\%C]_* = 0.598 + 2.57 \times 10^{-3}T + 0.063[\%Cr] \quad (3)$$

where, $[\%C]_*$ is the saturation solubility of C in metal, wt%,

T is the temperature, K.

If the initial content of Cr in metal is $[\%Cr]_0$, the expression of $[\%Cr]$ is:

$$\begin{aligned} [\%Cr] &= [\%Cr]_0 + 2 \left(\frac{W_s}{W_m} \frac{M_{Cr}}{M_{\text{Cr}_2\text{O}_3}} \right) \left[(\%Cr_2\text{O}_3)_0 - (\%Cr_2\text{O}_3) \right] \\ &= [\%Cr]_0 + \alpha \left[(\%Cr_2\text{O}_3)_0 - (\%Cr_2\text{O}_3) \right] \end{aligned} \quad (4)$$

where, $(\%Cr_2\text{O}_3)_0$ is the initial content of Cr_2O_3 in slag, wt%, $[\%Cr]_0$ is the initial Cr content in metal, wt%, W_s is the mass of slag, kg, W_m is the mass of metal, kg, M is the

mole mass, $\text{kg}\cdot\text{mol}^{-1}$ and $\alpha = 2 \left(\frac{W_s}{W_m} \frac{M_{Cr}}{M_{\text{Cr}_2\text{O}_3}} \right)$.

And $p_{\text{CO}} = 1$ atm, $K_1 = \frac{K\gamma_{\text{Cr}_2\text{O}_3}f_{\text{C}}^3}{f_{\text{Cr}}^2}$, then the mass transfer

equation represented by the mass fraction is obtained by the mathematical deduction.

$$\begin{aligned} \frac{d[\%Cr]}{dt} &= \frac{\alpha Fk_s\rho_s}{W_s} \left[\frac{[\%Cr]^2}{K_1(0.598 + 2.57 \times 10^{-3}T + 0.063[\%Cr])^3} \right. \\ &\quad \left. + \frac{[\%Cr] - [\%Cr]_0}{\alpha} - (\%Cr_2\text{O}_3)_0 \right] \end{aligned} \quad (5)$$

where, p_{CO} is the partial pressure of CO, atm, ρ_s is the density of slag, $\text{kg}\cdot\text{m}^{-3}$, K is the equilibrium constant of reaction, γ and f are the activity coefficients.

(2) Mass transfer of Cr in metal as the rate controlling step

The convective mass transfer equation of Cr in hot metal is:

$$\frac{dn_{\text{Cr}}}{dt} = Fk_m(C_{\text{Cr}_i} - C_{\text{Cr}}) \quad (6)$$

where, n_{Cr} is the mole number of Cr in metal, mol, k_m is the mass transfer coefficient of Cr in metal, $\text{m}\cdot\text{s}^{-1}$, C_{Cr_i} , C_{Cr} is the molar concentration of Cr at the interface and in metal respectively, $\text{mol}\cdot\text{m}^{-3}$.

The mass transfer equation represented by the mass fraction is obtained by the mathematical deduction.

$$\begin{aligned} \frac{d[\%Cr]}{dt} &= \frac{Fk_m\rho_m}{W_m} \left(\sqrt{K_1 \left((\%Cr_2\text{O}_3)_0 - \frac{1}{\alpha}([\%Cr] - [\%Cr]_0) \right)} \right. \\ &\quad \left. (0.598 + 2.57 \times 10^{-3}T + 0.063[\%Cr])^3 - [\%Cr] \right) \end{aligned} \quad (7)$$

where, ρ_m is the density of metal, $\text{kg}\cdot\text{m}^{-3}$.

(3) Chemical reaction at the interface as the rate controlling step

Assuming reaction (1) is a first-order reversible reaction, the reaction rate equation can be written as:

$$\frac{dn_{\text{Cr}}}{dt} = F(k_1 C_{\text{Cr}_2\text{O}_3,i} C_{\text{C}}^3 - k_{-1} C_{\text{Cr}_i}^2 p_{\text{CO}}) \quad (8)$$

where, k_1 , k_{-1} is the positive and negative reaction rate constant respectively, s^{-1} .

And the equilibrium constant $K = \frac{k_1}{k_{-1}}$, $p_{CO}=1$ atm, and the

mass transfer is quick, the interface concentration of each component is equal to the bath concentration, so Eq. (8) can be written as:

$$\frac{dn_{Cr}}{dt} = Fk_1(C_{Cr_2O_3}C_C^3 - C_{Cr}^2/K) \quad (9)$$

So the reaction rate equation represented by the mass fraction can be obtained by the mathematical deduction.

$$\frac{d[\%Cr]}{dt} = \frac{Fk_1\rho_m^2M_{Cr}}{100W_m} \left\{ \frac{\rho_m\rho_s}{10^4M_{Cr_2O_3}M_C^3} \left((\%Cr_2O_3)_0 - \frac{([\%Cr] - [\%Cr]_0)}{\alpha} \right) \right. \\ \left. (0.598 + 2.57 \times 10^{-3}T + 0.063[\%Cr])^3 - \frac{1}{KM_{Cr}^2} [\%Cr]^2 \right\} \quad (10)$$

(4) Mixed control conditions

If the resistance of each elementary step couldn't be neglected, the effects of them on the process must be considered simultaneously. In the quasi-stable state assumption, the speed of each elementary step is equal. R_{Cr} denotes the reduction reaction rate of chromium ore at the time of i , then

$$R_{Cr} = \frac{dn_{Cr_2O_3}}{dt} = 2 \frac{dn_{Cr}}{dt} \quad (11)$$

Accordingly, R_{Cr} can be obtained by the mathematical deduction under the conditions of the mixed control:

$$R_{Cr} = \frac{Fk_m}{k_1} \left[K\sqrt{\Delta} - Kk_m \left(1 + \frac{2k_1}{k_s} C_C^3 \right) - 2k_1 C_{Cr} \right] \quad (12)$$

where, $\Delta = k_m^2 \left(1 + \frac{2k_1}{k_s} C_C^3 \right) + 4 \frac{k_1}{K} \left(k_m C_{Cr} + \frac{2k_m k_1}{k_s} C_C^3 C_{Cr} + \right.$

$k_1 C_C^3 C_{Cr_2O_3} \left. \right)$, $C_{Cr} = \frac{[\%Cr]}{100M_{Cr}} \rho_m$, $C_C = \frac{[\%C]}{100M_C} \rho_m$, $C_{Cr_2O_3} =$

$\frac{(\%Cr_2O_3)}{100M_{Cr_2O_3}} \rho_s$, $(\%Cr_2O_3) = (\%Cr_2O_3)_0 - \frac{[\%Cr] - [\%Cr]_0}{\alpha}$,

$n_{Cr} = \frac{[\%Cr]W_m}{100M_{Cr}}$; $\alpha = 2 \left(\frac{W_s}{W_m} \frac{M_{Cr}}{M_{Cr_2O_3}} \right)$.

The system of equations mentioned above can be solved using the method of Runge-Kutta numerical differentiation. The relational curve of $[\%Cr]$ and time can be obtained under the conditions of mixed control.

3. Mathematical Modeling for Dissolution and Reduction of Chromium Ore in Converter

The dissolution behavior of chromium ore in CaO-SiO₂-

MgO-Al₂O₃ slag system was studied in the laboratory¹²⁾ and the kinetic model for dissolution process of chromium ore was developed.¹³⁾

When the dissolution and reduction of chromium ore reach equilibrium, it is assumed that the radius of chromium ore particle is calculated according to the average particle size and the specific surface area of chromium ore in slag is constant. So the dissolution rate of chromium ore in smelting reduction converter at the time of i (R_{Si}) can be expressed by Eq. (13):

$$R_{Si} = \frac{3W_{ore}}{r_0 \times \rho_p} \cdot k_r (C_{Cr_2O_3*} - C_{Cr_2O_3i}) \quad (13)$$

where, k_r is the apparent rate constant of dissolution reaction, $C_{Cr_2O_3i}$ is the molar concentration of Cr₂O₃ at the surface of chromium ore, mol·m⁻³, $C_{Cr_2O_3*}$ is the molar concentration of Cr₂O₃ for saturation solubility in slag, mol·m⁻³, W_{ore} is the mass of chromium ore, kg, r_0 is the initial radius of chromium ore particle, m, ρ_p is the density of chromium ore, kg·m⁻³.

According to the literature,¹¹⁾ the saturation solubility of Cr₂O₃ in slag $[(Cr_2O_3)*]$ can be written as:

$$(\%Cr_2O_3)_* = 8.30 \times 10^{-3}T - 12.1 \quad (14)$$

When stopping injecting chromium ore, the specific surface area of chromium ore in slag reduces gradually with the reduction time. At the moment, the dissolution rate of chromium ore can be expressed by the following equations:

$$R_{Si} = 4\pi r_i^2 N_{ore} k_r (C_{Cr_2O_3*} - C_{Cr_2O_3i}) \quad (15)$$

$$-\frac{dr_i}{dt} = \frac{1}{\rho_p} k_r (C_{Cr_2O_3*} - C_{Cr_2O_3i}) \quad (16)$$

where, N_{ore} is the numbers of chromium ore particles, r_i is the radius of chromium ore particle of i , m, k_r is the apparent rate constant of dissolution reaction, in which e represents exponential function, R is the basicity of the slag.

$$k_r = 1.4094 - 0.2113e^R + 0.0247e^{2R} + 0.1374 \ln(\%MgO) + \\ 0.0343 \ln^2(\%MgO) + 0.7165 \ln(\%Al_2O_3) + \\ 0.2081 \ln^2(\%Al_2O_3) + 1.0390 \times 10^{13} e^{-63067.71/T} + \\ 0.0024(\%CaF_2) + 0.0003(\%CaF_2)^2 \quad (12)$$

As the dissolution and reduction of chromium ore go on simultaneously, the molar concentration of Cr₂O₃ in slag and the molar concentration of chromium in metal at the time of $i+1$ within the time step of $\Delta\tau$ are as follows, respectively:

$$C_{Cr_2O_3i+1} = C_{Cr_2O_3i} + \frac{(R_{Si} - R_{Cri})}{V_s} \times \Delta\tau \quad (17)$$

$$C_{Cri+1} = C_{Cri} + \frac{R_{Cri}}{V_m} \times \Delta\tau \quad (18)$$

where, V_s is the volume of the slag, m³, V_m is the volume of the metal, m³.

The system of simultaneous Eqs. (12)–(18) mentioned above can be solved by the self-programming procedure, and the relational curve of every variable in the coupling dynamic model and time can be obtained.

4. Determination of Model Parameters

4.1. Equilibrium Constant K

The relational expression between equilibrium constant of Eq. (1) and temperature can be got according to the related thermodynamic data¹⁴⁾ including the standard solution free energy change of each component in hot metal.

$$\log K = -\frac{37608.7}{T} + 24.143 \quad \text{..... (19)}$$

The working temperature of the process for chromium ore smelting reduction is set to be 1560°C (1833 K), so K is equal to 4.223×10^3 by solving Eq. (19).

4.2. Mass Transfer Coefficient k_m and k_s

Owing to the lack of the data concerning the mass transfer character of molten slag with chrome, the data from dynamic model of instant and persistent contact reactions established by Robertson are adopted, namely k_m is equal to 2.4×10^{-3} – $4.6 \times 10^{-3} \text{ m}\cdot\text{s}^{-1}$.¹⁵⁾ Here $4.0 \times 10^{-3} \text{ m}\cdot\text{s}^{-1}$ is selected ($k_m = 4.0 \times 10^{-3} \text{ m}\cdot\text{s}^{-1}$). Some researches indicate that the effect of temperature and stirring energy on k_m/k_s is similar approximately, namely the value of k_m/k_s is invariable at different temperature and stirring energy.¹⁶⁾ In the coupling dynamic models for slag-metal and slag-metal-gas established by Robertson, k_m/k_s is equal to 1–10.¹⁷⁾ Here 8 is selected ($k_m/k_s = 8$), namely $k_s = 5.0 \times 10^{-4} \text{ m}\cdot\text{s}^{-1}$.

4.3. Other Parameters

The density of metal and slag (ρ_m and ρ_s) are $7.0 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$ and $3.5 \times 10^3 \text{ kg}\cdot\text{m}^{-3}$, respectively. The mass of metal is $1.5 \times 10^5 \text{ kg}$ and the mass of slag is $3.3 \times 10^4 \text{ kg}$. The initial content of Cr_2O_3 ($(\% \text{Cr}_2\text{O}_3)_0$) in slag is 3.114 wt%. According to the operating conditions and research results of top-bottom combined blowing converter, the interfacial area between slag and metal estimates to be 0.6 – $1.7 \text{ m}^2\cdot\text{kg}^{-1}$.¹⁸⁾ Because the quantity of slag for chromium ore smelting reduction is relatively great, the upper limit $1.7 \text{ m}^2\cdot\text{kg}^{-1}$ is selected in this model, namely $F = 2.55 \times 10^5 \text{ m}^2$.

5. Modeling Verification

Using the coupling dynamic model for the process of

chromium ore smelting reduction in a converter, the time needed for refining stainless steel crude melts with target chromium content is predicted. Then the calculated refining time by the mathematical model is compared with the actual refining time of JFE so as to verify the accuracy of coupling dynamic model. According to the blowing conditions of JFE smelting reduction converter,¹⁹⁾ the following parameters are selected: the operating temperature is 1560°C, the charge amount of stainless scrap and recycled metal with chromium are $190 \text{ kg}\cdot\text{t}^{-1}$ and $250 \text{ kg}\cdot\text{t}^{-1}$, respectively, and the added quantity of chromium ore is $230 \text{ kg}\cdot\text{t}^{-1}$. Namely the initial chromium content in metal ($[\% \text{Cr}]_0$) is 5.8 wt%, the chromium content in final slag is 1.0 wt%.

The time needed for refining 185 t stainless steel crude melts with 12 wt% Cr is calculated using the coupling dynamic model for the process of chromium ore smelting reduction in a converter, and the calculation result is shown in Fig. 1. The calculated result of model shows that it takes 90 min to refine 12 wt% Cr stainless steel crude melts, and the actual time needed for refining 9–12 wt% Cr stainless steel crude melts in the 185 t smelting reduction converter of No. 4 steelmaking shop at Chiba Works, JFE is 85–88 min.¹⁹⁾ That is to say, the calculated time is in general agreement with the actual refining time under the same conditions.

For further verifying the coupling dynamic model, the computed profile of the chromium content in metal with time (Fig. 2) is compared with the measured profile of that in the smelting reduction furnace of No. 1 steelmaking shop at Chiba Works, JFE (Fig. 3).²⁰⁾ The computational conditions used in this study are listed in Table 1.

Comparing Fig. 2 with Fig. 3, the computed $[\% \text{Cr}]$ curve is found to be similar to the actual production curve. The difference between computed and measured values during smelting reduction period appears to be because Cr ore is sandy in the computational conditions, which is an advantage in terms of the reaction interfacial area, while Cr pellets are lumpy in form, used in the smelting reduction furnace of No. 1 steelmaking shop at Chiba Works. The comparison between computational results and actual production data demonstrates the validity of the model. So it is concluded that the established coupling dynamic model can be used to describe and resolve the process of producing stainless steel

Fig. 1. Relationship between $[\% \text{Cr}]$ and time during smelting reduction of chromium ore ($[\% \text{Cr}]_0 = 5.8 \text{ wt}\%$).

Fig. 2. Relationship between $[\% \text{Cr}]$ and time during smelting reduction of chromium ore ($[\% \text{Cr}]_0 = 0.0 \text{ wt}\%$).

Fig. 3. Change in chemical composition and temperature of molten bath in the smelting reduction furnace of No. 1 steelmaking shop at Chiba Works, JFE.

Table 1. Standard computational conditions of coupling dynamic model used in this study

Parameters / Unit		Value
Raw material	Blowing quantity of chromium ore / ($\text{kg} \cdot \text{t}^{-1}$)	410
	Charge amount of stainless scrap / ($\text{kg} \cdot \text{t}^{-1}$)	0
	Charge amount of recycled metal / ($\text{kg} \cdot \text{t}^{-1}$)	0
	Average particle size of chromium ore / mm	1.5
Operating conditions	Operating temperature (T) / °C	1560
	Initial chromium content in metal ($[\% \text{Cr}]_0$) / %	0
	Chromium content in final slag (T[Cr]) / %	1.0
	Mass of stainless steel crude melt / t	150
	(%CaO)/(%SiO ₂)	1.2
Slag composition	(%Al ₂ O ₃) / %	15
	(%MgO) / %	10
Tapping composition	$[\% \text{Cr}]$ / %	12

crude melts by chromium ore smelting reduction in a converter.

6. Calculation Results and Discussion

6.1. Effect of Initial Chromium Content in Hot Metal on Refining Time of Smelting Reduction Converter

Under the computational conditions of Table 1, the established coupling dynamic model is calculated, and the variation of chromium content in hot metal with time at the different initial chromium content can be obtained, as shown in Fig. 4. When the initial chromium content in hot metal is 0.0 wt%, 2.2 wt% and 5.8 wt% respectively, the calculated time for refining 12 wt% Cr stainless steel crude melts in the 150 t smelting reduction converter is 121 min, 100 min and 78 min respectively. Accordingly, the average injecting rate of chromium ore is $467 \text{ kg} \cdot \text{min}^{-1}$, $431 \text{ kg} \cdot \text{min}^{-1}$ and $338 \text{ kg} \cdot \text{min}^{-1}$ respectively.

That is to say, the refining time reduces greatly when the initial chromium content in hot metal increases. Consequently, some recycled Cr-bearing metals are added to the hot metal before injecting chromium ore so as to shorten the

Fig. 4. Effect of initial chromium content in hot metal on refining time of smelting reduction converter. 1–0.0 wt%, 2–2.2 wt%, 3–5.8 wt%.

Fig. 5. Effect of particle size of chromium ore on $[\% \text{Cr}]$ ($[\% \text{Cr}]_0=0.0 \text{ wt}\%$). 1–0.278 mm, 2–1.5 mm, 3–3 mm.

refining time and improve the production efficiency of the smelting reduction converter.

6.2. Effect of Particle Size of Chromium Ore on Smelting Reduction Process

Under the same computational conditions as Table 1 but changing the particle size of chromium ore, the effect of chromium ore particle sizes of 0.278 mm, 1.5 mm and 3 mm on the smelting reduction process is researched, and the computing results are shown in Figs. 5–8.

The effect of particle size on the initial dissolution rate of chromium ore is relatively great, as shown in Fig. 8(a). When the particle size of chromium ore is 0.278 mm, 1.5 mm and 3 mm respectively, the contents of chromium oxide in slag increase rapidly to be nearly saturated in less than 1 min, 4 min and 11 min respectively. However, the change of particle size has minimal impact on the reduction rate of chromium ore, as shown in Fig. 6. So the calculated times for refining 12 wt% Cr stainless steel crude melts in the 150 t smelting reduction converter are almost equal at the different particle sizes of chromium ore, as shown in Fig. 5.

Under the conditions of the coupling calculation, it is concluded that the dissolution process of chromium ore in slag is not rate controlling step and the smelting reduction rate is dominated mainly by the reduction of chromium ore,

when the particle size of chromium ore is 0.278–3 mm. S. Yokoyam *et al.*⁸⁾ studied the smelting reduction behavior of chromium ore in molten slag of (CaO)–(SiO₂)–(Al₂O₃)–(MgO) system by carbon in liquid iron held in graphite crucible at 1390°C–1680°C. The average size of chromium ore is 0.158 mm. The reduction rate was expressed by a zero-order equation at an early stage of smelting reduction. During this stage, both (CrO) and the rate were kept constant and unaffected by the dissolution of the ore into slag. S. Kitamura *et al.*²¹⁾ estimated the smelting reduction rate of Cr-ore in top-and-bottom blowing converter by 600 kg scale fundamental experiment and 100 t scale industrial furnace (LD-OB). The change of Cr oxide in slag with time showed zero-order reaction kinetics. The rate was not clearly affected by the kind of Cr-sources (chromium ore size is 0.1–1.0 mm) and the reduction of chromium ore was the rate controlling step. These findings are basically consistent with the obtained conclusion above of this paper.

Consequently, we should take measures to increase the reduction rate of chromium ore at the moment. The conclusions of the dynamic model for interfacial reaction between the slag and the metal show that the rate and the efficiency of the interfacial reducing reaction of chromium ore can be improved by increasing the mass ratio of the slag and metal (*e.g.*, the operation of great slag quantity and thick slag blanket),²²⁾ the interfacial area between the slag and the metal (*e.g.*, the reinforcement of the molten bath stirring), the

mass transfer coefficient of chromium oxide in the slag (*e.g.*, the adjustment of the slag viscosity) and so on.

Under the same computational conditions but changing the particle size of chromium ore, the effect of larger particle sizes of chromium ore of 10 mm and 20 mm on the smelting reduction process is researched, and the computing results are shown in Figs. 9–11.

When the particle size of chromium ore increases to 10 mm and more, the changing of particle size has the significant effects on both of the reduction rate and the dissolution rate of chromium ore, as shown in Figs. 10 and 11. When the particle size of chromium ore is 10 mm and 20 mm respectively, the content of chromium in metal is only 10.1 wt% and 7.5 wt% respectively at the refining time of 121 min, as shown in Fig. 9.

When the particle size of chromium ore increases to some fixed value (*e.g.* 10 mm), the changing of particle size has the significant effect on the smelting reduction process of chromium ore under the conditions of the coupling calculation. At the moment, the dissolution process of chromium ore in slag is the rate controlling step at a certain stage of the smelting reduction and the smelting reduction process is controlled jointly by the dissolution and reduction of chromium ore. T. Takaoka *et al.*²³⁾ carried out the experiments on the smelting reduction of chromium ore in BOF and showed that the finer the chrome ore size, the higher the

Fig. 6. Effect of particle size of chromium ore on reduction rate R_{Cr} ([%Cr]₀=0.0 wt%). 1–0.278 mm, 2–1.5 mm, 3–3 mm.

Fig. 7. Effect of particle size of chromium ore on dissolution rate R_S ([%Cr]₀=0.0 wt%). 1–0.278 mm, 2–1.5 mm, 3–3 mm.

Fig. 8. Partial enlarged drawing of Fig. 7 ([%Cr]₀=0.0 wt%) (a) 0–5 min, (b) 15–121 min. 1–0.278 mm, 2–1.5 mm, 3–3 mm.

Fig. 9. Effect of particle size of chromium ore on [%Cr] ([%Cr]₀=0.0 wt%). 1–1.5 mm, 2–10 mm, 3–20 mm.

Fig. 12. Effect of temperature on [%Cr] ([%Cr]₀=0.0 wt%). 1–1 813 K, 2–1 833 K, 3–1 853 K.

Fig. 10. Effect of particle size of chromium ore on reduction rate R_{Cr} ([%Cr]₀=0.0 wt%). 1–1.5 mm, 2–10 mm, 3–20 mm.

Fig. 13. Effect of temperature on reduction rate R_{Cr} ([%Cr]₀=0.0 wt%). 1–1 813 K, 2–1 833 K, 3–1 853 K.

Fig. 11. Effect of particle size of chromium ore on dissolution rate R_S ([%Cr]₀=0.0 wt%). 1–1.5 mm, 2–10 mm, 3–20 mm.

Fig. 14. Effect of temperature on dissolution rate R_S ([%Cr]₀=0.0 wt%). 1–1 813 K, 2–1 833 K, 3–1 853 K.

reduction rate. That is to say, the reduction rate of chromium ore is affected by its dissolution, which shows the agreement with the rate controlling step proposed above in this paper.

Consequently, it is concluded that the chromium ore sand, whose particle size is 0–3 mm, can satisfy the dissolution request and has a faster reduction rate. In the practical refining process, the use of chromium ore powder can increase the fume amount of the smelting reduction converter and reduce the chromium yield. So it is suggested that smelting reduction converter should use chromium ore sand as raw material and an exclusive-use lance for chromium ore charge-

ing should be adopted for direct addition of Cr ore sand into the furnace with good yield in order to ensure the smelting reduction rate of chromium ore and the chromium yield.

6.3. Effect of Temperature on Smelting Reduction Process

Figures 12–14 show the effect of temperatures of 1 540°C, 1 560°C and 1 580°C on the smelting reduction process of chromium ore in a converter. The change of temperature has the great effects on both of the dissolution rate (R_S) and the reduction rate (R_{Cr}) of chromium ore. When the

temperature is 1540°C, 1560°C and 1580°C respectively, the mean reduction rate of chromium ore is 0.052 wt%·min⁻¹, 0.091 wt%·min⁻¹ and 0.175 wt%·min⁻¹ respectively. Accordingly, the average injecting rate of chromium ore is 267 kg·min⁻¹, 467 kg·min⁻¹ and 897 kg·min⁻¹ respectively.

When the temperature is 1540°C, the chromium content in metal is only 7 wt% at the refining time of 121 min. The calculated time for refining 12 wt% Cr stainless steel crude melts in the 150 t smelting reduction converter is only 55 min at the temperature of 1580°C. So the effect of temperature on the smelting reduction process of chromium ore is very notable. But too high a temperature can reduce the campaign life of the converter and enhance the cost of fettling and patching.

The smelting reduction process of the chromium ore in a converter includes the dissolution of chromium ore in slag and the reduction of chromium oxide in slag. The chromium oxide in slag increases with the dissolution of chromium ore and decreases due to the reducing reaction. Correspondingly, the dissolution and reduction of chromium ore influence the total chromium content in slag, which in turn affects the dissolution rate and reduction rate. That is to say, the dissolution and reduction of chromium ore are the coupling process of acting on and influencing each other. This is the reason why R_{Cr} and R_S have the behavior in the above figures.

7. Conclusions

Basing on the kinetic models of chromium ore dissolution and interfacial reducing reaction between the slag and metal, the coupling dynamic model for the process of chromium ore smelting reduction in a converter is established for the first time. Under the calculation conditions of the coupling dynamic model, the following conclusions are obtained.

(1) When the initial chromium content in hot metal is 0.0 wt%, 2.2 wt% and 5.8 wt% respectively, the calculated time for refining 12 wt% Cr stainless steel crude melts in the 150 t smelting reduction converter is 121 min, 100 min and 78 min respectively at 1560°C. Accordingly, the average injecting rate of chromium ore is 467 kg·min⁻¹, 431 kg·min⁻¹ and 338 kg·min⁻¹ respectively. The refining time reduces greatly with increasing the initial chromium content in hot metal.

(2) When the particle size of chromium ore is smaller (e.g. less than 3 mm), the dissolution process of chromium ore in slag is not rate controlling step and the smelting reduction rate is dominated mainly by the reduction of chromium ore. When the particle size of chromium ore increases to some fixed value (e.g. 10 mm), the changing of particle size has the significant effect on the smelting reduction process of chromium ore. At the moment, the dissolution process

of chromium ore in slag is rate controlling step at a certain stage of the smelting reduction and the smelting reduction process is controlled jointly by the dissolution and reduction of chromium ore.

(3) The effect of temperature on the smelting reduction process of chromium ore is very notable. When the temperature is 1540°C, 1560°C and 1580°C respectively, the mean reduction rate of chromium ore is 0.052 wt%·min⁻¹, 0.091 wt%·min⁻¹ and 0.175 wt%·min⁻¹ respectively. Accordingly, the average injecting rate of chromium ore is 267 kg·min⁻¹, 467 kg·min⁻¹ and 897 kg·min⁻¹ respectively.

Acknowledgments

This work is supported by the Open Subject Fund of the State Key Laboratory of Rolling and Automation of NEU, China (No.2009003) and the National Natural Science Foundation of China (50904017) and the Project for Liaoning Provincial Scientific Research in University of China (No. L2011210).

REFERENCES

- 1) O. Soykan, R. H. Eric and R. P. King: *Metall. Trans. B*, **22B** (1991), 801.
- 2) C. Vercruyssen, P. Wollants and J. R. Roos: *Ironmaking Steelmaking*, **21** (1994), 287.
- 3) X. B. Zhang, G. C. Jiang and K. D. Xu: *J. East China Univ. Metall.*, **14** (1997), 214.
- 4) K. P. D. Perry, C. W. P. Finn and R. P. King: *Metall. Trans. B*, **19B** (1988), 677.
- 5) W. G. Pei and O. Wijk: *Scand. J. Metall.*, **22** (1993), 38.
- 6) R. J. Fruchan: *Metall. Trans. B*, **8B** (1977), 429.
- 7) H. G. Katayama, M. Satoh and M. Tokuda: *Tetsu-to-Hagané*, **75** (1989), 1883.
- 8) S. Yokoyama, M. Takeda and H. Oogusu: *Tetsu-to-Hagané*, **78** (1992), 215.
- 9) M. Kawakami, Y. Kitajima and K. Hashimoto: *Trans. Iron Steel Inst. Jpn.*, **27** (1987), 176.
- 10) Y. L. Ding and A. J. Merchant: *Ironmaking Steelmaking*, **26** (1999), 254.
- 11) Y. P. Xiao: Fundamental research of smelting reduction, master thesis, Northeastern University, Shenyang, (1988).
- 12) M. F. Jiang, Y. Liu and D. Y. Wang: Proc. of TMS 137th Annual Meeting & Exhibition, Minerals, Metals & Materials Society, Warrendale, PA, (2008), 201.
- 13) Y. Liu, M. F. Jiang and D. Y. Wang: *J. Northeastern Univ. : Nat. Sci.*, **28** (2007), 830.
- 14) Y. J. Liang and Y. C. Che: Thermodynamic Data Manual of Inorganic Matters, Northeastern University Press, Shenyang, (1993).
- 15) S. Ohguchi and D. G. C. Robertson: *Ironmaking Steelmaking*, **11** (1984), 262.
- 16) S. Kitamura and T. Kitamura: *ISIJ Int.*, **31** (1991), 1322.
- 17) D. G. C. Robertson, B. Deo and S. Ohguchi: *Ironmaking Steelmaking*, **11** (1984), 41.
- 18) Y. Qu: Principle of Steelmaking, Metallurgy Industry Press, Beijing, (1980).
- 19) Y. Kishimoto, K. Taoka and S. Takeuchi: *Kawasaki Steel Tech. Rep.*, **28** (1996), 213.
- 20) M. Nishikoori, H. Nishikawa and K. I. Sorimachi: *Kawasaki Steel Tech. Rep.*, **25** (1993), 79.
- 21) S. Kitamura, T. Arai, M. Matsuo, N. Sato, K. Okohira and H. Ishikawa: *Tetsu-to-Hagané*, **74** (1988), 672.
- 22) H. Katayama, T. Ibaraki and T. Ohno: *ISIJ Int.*, **33** (1993), 124.
- 23) T. Takaoka: *Tetsu-to-Hagané*, **72** (1986), S111.